

(19) Japan Patent Office (JP)

(12) Publication of Patent Application (A)

(11) Publication Number of Patent Application: H10-125463

(43) Date of Publication: H10, May 15 (1998.5.15)

5 (51) Int. Cl.<sup>6</sup> Identification Mark FI  
H05B 33/04 H05B 33/04  
F21V 8/00 601 F21V 8/00 601A  
G02F 1/1335 530 G02/F 1/1335 530  
H05B 33/06 H05B 33/06  
10 33/10 33/10

Request for Examination: Not made Number of Claims: 30 OL (Total Pages: 21)

Continued on the last page

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(21) Application Number: H8-344831

(22) Application Date: H8, December 25 (1996.12.25)

15 (31) Priority Application Number: H7-342827

(32) Priority Date: H7, December 28 (1995. 12. 28)

(33) Priority Country: Japan (JP)

(31) Priority Application Number: H8-230022

(32) Priority Date: H8, August 30 (1996. 8. 30)

20 (33) Priority Country: Japan (JP)

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5 (54) [Title of the Invention] ORGANIC ELECTROLUMINESCENT ELEMENT,  
LIQUID CRYSTAL LIGHTING SYSTEM, DISPLAY DEVICE, AND  
MANUFACTURE OF ORGANIC ELECTROLUMINESCENT ELEMENT

(57) [Abstract]

[Object] To provide an organic electroluminescent element having excellent durability  
10 and reliability, a manufacturing method with mass productivity, and a device using this.  
[Means for solution] By bonding a shield member to a substrate using low-melting glass,  
a low-melting solder, or the like, intrusion of moisture and oxygen into a cathode and an  
organic thin film layer is blocked, so that high reliability is obtained. The shield member  
8 is locally heated using a laser or an ultrasonic wave in order to melt the shield member 8,  
15 whereby the bonding can be certainly conducted without thermal destruction of an  
organic thin film layer 3. An anode 2 and the organic thin film layer 3 are solidly bonded  
through a carbon so that reliability of light-emitting characteristics is improved, and a  
lead line and the cathode are covered with a material with excellent conductivity. As a  
result, light-emitting efficiency is increased. When an Al based alloy containing Mg,  
20 Mg and Li, Mn, or Mn and Li is used as a material of the cathode 6, corrosion resistance  
of the cathode 6 is increased.

[Scope of Claims]

[Claim 1] An organic electroluminescent element comprising:

25 a substrate;  
a stacked structure including an anode, an organic thin film layer, a cathode  
stacked on the substrate;  
a shield member provided on the substrate to cover an outer surface side of the  
stacked structure; and  
30 an adhesive member provided between the substrate and the shield member.

[Claim 2] The organic electroluminescent element according to Claim 1, characterized in that the anode, the organic thin film layer, and the cathode are stacked in this order on the substrate.

[Claim 3] The organic electroluminescent element according to Claim 1 or 2,  
5 characterized in that a part of or the whole anode is made of a carbon thin film.

[Claim 4] The organic electroluminescent element according to Claim 1, characterized in that the stacked structure is formed by stacking an anode, a carbon thin film, an organic thin film layer, and a cathode on the substrate.

[Claim 5] The organic electroluminescent element according to Claim 1,  
10 characterized in that an anode, a carbon thin film, an organic thin film layer, a cathode are stacked in this order on the substrate.

[Claim 6] The organic electroluminescent element according to any one of Claims 1 to 5, characterized in that at least a part of the adhesive member bonds the substrate and the shield member.

[Claim 7] The organic electroluminescent element according to any one of Claims 1 to 6, characterized in that the organic thin film layer emits light when voltage is applied to the anode and the cathode.

[Claim 8] The organic electroluminescent element according to any one of Claims 1 to 7, characterized in that the substrate is made of any one of a transparent substrate and  
20 a semi-transparent substrate.

[Claim 9] The organic electroluminescent element according to any one of Claims 1 to 8, characterized in the adhesive member is made from any one of low-melting glass, a low-melting solder, and liquid crystal polymer.

[Claim 10] The organic electroluminescent element according to any one of Claims 1 to 9, characterized in that the adhesive member has a melting point of 500 °C or less.

[Claim 11] The organic electroluminescent element according to Claim 9, characterized in that the low-melting glass is made from any one of low-melting glass a Pb-B-Sn-Si-Al-O compound, a Sn-Pb-O-F compound, a Pb-Sn-P-O-Cl compound, and a PbO-SnO-P<sub>2</sub>O<sub>5</sub> compound.

[Claim 12] The organic electroluminescent element according to any one of Claims

1 to 11, characterized in that the shield member is formed from any one of electric insulating glass and stainless steel.

[Claim 13] The organic electroluminescent element according to Claim 12, characterized in that the shield member has a gap shape.

5 [Claim 14] The organic electroluminescent element according to any one of Claims 1 to 13, characterized in that a protective film is provided to cover the stacked structure between the stacked structure and the shield member.

[Claim 15] The organic electroluminescent element according to Claim 14, characterized in that the adhesive member is made from a low-melting solder, and the  
10 protective film is an electric insulating compound layer and electrically separates the anode and the cathode.

[Claim 16] The organic electroluminescent element according to Claim 14, characterized in that a film thickness of the protective film is 3  $\mu\text{m}$  to 30  $\mu\text{m}$ .

[Claim 17] The organic electroluminescent element according to Claims 14,  
15 characterized in that the protective film is a stacked film of at least two or more layers including an insulating compound layer in a lowest layer and a metal layer in a top layer.

[Claim 18] The organic electroluminescent element according to any one of Claims 1 to 17, characterized in that an electric insulating buffer layer is provided on an adhesive surface of at least one of the substrate and the shield member.

20 [Claim 19] The organic electroluminescent element according to Claim 18, characterized in that the electric insulating buffer layer is any one of  $\text{SiO}_2$  and  $\text{SiO}$ .

[Claim 20] The organic electroluminescent element according to any one of Claims 1 to 19, characterized in that the cathode is made of any one of an Al based alloy containing Mg, an Al based alloy containing Mg and Li, an Al based alloy containing Mn,  
25 and an Al based alloy containing Mn and Li.

[Claim 21] An organic electroluminescent element component, characterized by comprising:

the organic electroluminescent element according to any one of Claims 1 to 20;

an electrode driver IC provided on the substrate in order to drive the anode and

30 the cathode; and

a lead line provided on the substrate in order to connect the electrode driver IC.

[Claim 22] The organic electroluminescent element component according to Claim 21, characterized in that the lead line has a stacked structure, and conductivity of an upper layer is higher than conductivity of a lower layer.

5 [Claim 23] The organic electroluminescent element component according to Claim 21 or 22, characterized in that the cathode has a stacked structure, and conductivity of an upper layer is higher than conductivity of a lower layer.

[Claim 24] A liquid crystal lighting system comprising:

the organic electroluminescent element according to any one of Claims 1 to 20;  
10 means for driving the anode and the cathode; and  
a liquid crystal panel provided on a front face side of the organic electroluminescent element,  
characterized in that lighting is conducted by applying voltage to the organic electroluminescent element.

15 [Claim 25] A display device comprising:

the organic electroluminescent element according to any one of Claims 1 to 20;  
means for driving the anode and the cathode; and  
a liquid crystal panel provided on a front face side of the organic electroluminescent element,  
20 characterized in that display function is performed by applying matrix voltage to the organic electroluminescent element.

[Claim 26] A method for manufacturing an organic electroluminescent element comprising the steps of:

a step for forming a stacked structure by stacking an anode, an organic thin film  
25 layer, and a cathode on a substrate;  
a step for providing a shield member to cover an outer surface side of the stacked structure on the substrate through an adhesive member;  
a step for melting the adhesive member; and  
a step for bonding the substrate and the shield member using the melted adhesive  
30 member.

[Claim 27] The method for manufacturing an organic electroluminescent element according to Claim 26, characterized in that the step for forming a stacked structure is a step for stacking an anode, a carbon thin film, an organic thin film, and a cathode on a substrate.

5 [Claim 28] The method for manufacturing an organic electroluminescent element according to Claim 26 or 27, characterized in that the substrate is a transparent or semi-transparent substrate.

[Claim 29] The method for manufacturing an organic electroluminescent element according to any one of Claims 26 to 28, characterized in that the adhesive member is  
10 made from any one of low-melting glass, a low-melting solder, and liquid crystal polymer.

[Claim 30] The method for manufacturing an organic electroluminescent element according to any one of Claims 26 to 29, characterized in that the step for melting an adhesive member is a step for melting the adhesive member using laser process or a step  
15 for melting the adhesive member using an ultrasonic wave.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

20 The present invention relates to an organic electroluminescent element that is an electrical light-emitting element used for a light-emitting source for a liquid crystal display, a light-emitting source for a backlight of a display, or a light-emitting source for display and optical communication. The present invention also relates to a device using the organic electroluminescent element and a method for manufacturing the organic  
25 electroluminescent element.

[0002]

[Prior Art]

An electroluminescent element is a light-emitting device utilizing electroluminescence of a solid fluorescent substance or a phenomenon that is called  
30 electroluminescence. Nowadays, inorganic electroluminescent elements using an

inorganic material as a luminous body are put into practice, and its application expansion into a backlight of a liquid crystal display, a flat display, or the like has been attempted. However, the inorganic electroluminescent elements have defects that a high AC voltage of 100 V or more is needed to make the element emit light, and blue emission is difficult; therefore, full color display by three primary colors of R.G.B, that is, Red, Green, and Blue, is difficult.

[0003]

On the other hand, electroluminescent elements using an organic material have been researched from a long time ago, but they are very inefficient, and only low luminance can be obtained; therefore, the research thereof has failed to reach actual practical use. However, a structure, in other words, an organic electroluminescent element having a function-separated stacked structure in which an organic substance is separated into two layers of a hole transporting layer and a light-emitting layer 5, achieved light emission with high luminance of  $1000 \text{ cd/m}^2$  or more regardless of at low voltage of 10 V or less, which was proposed by C.W. Tang and the like of Eastman Kodak Company in 1987. (C.W. Tang and S.A.Vanslyke: Appl. Phys. Lett, 51 (1987) 913) Incidentally, "cd" is an abbreviated name of candela. As a result, organic electroluminescent elements were suddenly attracted attention. In recent years, organic electroluminescent elements having a similar structure have been actively researched.

[0004]

Here, a structure of a conventional organic thin film electroluminescent element is briefly described with reference to FIG. 15. FIG. 15 is a cross-sectional view of an essential part of the conventional organic electroluminescent element.

[0005]

In FIG. 15, reference numeral 1 denotes a substrate 1; 2, an anode 2; 3, an organic thin film layer 3; 4, a hole transporting layer 4; 5, a light-emitting layer 5; and 6, a cathode 6.

[0006]

The conventional organic electroluminescent element as shown in FIG. 15 is provided with the followings: the transparent or semi-transparent substrate 1 such as

glass; the anode 2, which is made of a transparent conductive film such as ITO by a sputtering method, an evaporation method, or the like on the substrate 1; the hole transporting layer 4 formed by an evaporation method or the like on the anode 2, which is made of TPD, that is, *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (hereinafter, abbreviated as TPD) or the like; the light-emitting layer 5 formed by an evaporation method or the like on the hole transporting layer 4, which is made of 8-Hydroxyquinoline Aluminum (hereinafter, abbreviated as Alq<sub>3</sub>); and the cathode 6 formed by an evaporation method or the like on the light-emitting layer 5, which is made of a metal film or the like. The cathode 6 is generally made of a metal film with low work function such as AlLi, MgAg, or the like.

[0007]

The organic thin film layer 3 in the organic electroluminescent element shown in FIG. 15 comprises the hole transporting layer 4 and the light-emitting layer 5.

15 [0008]

When DC voltage or DC current is applied on the conditions that the anode 2 is a plus pole and the cathode 6 is a minus pole in the organic electroluminescent element having the above structure, holes are injected from the anode 2 to the light-emitting layer 5 through the hole transporting layer 4, and electrons are injected from the cathode 6 to the light-emitting layer 5. In the light-emitting layer 5, the holes and the electrons are recombined, and excitons are caused by the recombination. When the excitons transfer from the excited state to the ground state, a light-emission phenomenon is generated. By changing a layer structure of the organic thin film layer 3 and a material used for the light-emitting layer 5, a light emission wavelength can be changed. In order to improve light-emitting characteristics of such an organic electroluminescent element, the followings have been studied: 1) improvement of a structure of the organic thin film layer 3 including the light-emitting layer 5, a hole transporting layer 4, and the like and an organic material used therefore; or 2) improvement of a material used for the anode 2 and the cathode 6.

30 [0009]



For example, as for 2), for the purpose of lowering a barrier between the cathode 6 and the light-emitting layer 5 so as to make the electrons easy to be injected to the light-emitting layer 5, a material with low work function and high electric conductivity has been proposed, such as a Mg-Ag alloy described in United State Patent No. 4885211 or an Al-Li alloy described in Japanese Published Patent Application No. H5-121172. Such materials are widely used still now.

[0010]

[Problems to be solved by the Invention]

However, these alloy materials have high activity and are unstable chemically; therefore, corrosion and oxidation are caused by reaction with moisture and oxygen in the air. Such corrosion and oxidation of the cathode 6 make a portion where light is not emitted, called a dark spot in the light-emitting layer 5, greatly grow, which is a cause of characteristic deterioration over time in the organic electroluminescent element.

[0011]

Further, this is not limited to the cathode 6, and an organic material used for the organic thin film layer 3 such as the light emitting layer 5 and the hole transporting layer 4 is to cause growth of a dark spot because the structure is changed by reaction with moisture and oxygen in general.

[0012]

Accordingly, in order to improve durability and reliability of the organic electroluminescent element, reaction between materials used for the cathode 6 and the organic thin film layer 3 and moisture and oxygen is prevented, so that the whole of the organic electroluminescent element is needed to be sealed.

[0013]

As for sealing the organic electroluminescent element, two methods have been mainly examined until now. One of them is to form a protective film on an outer surface of the organic electroluminescent element using a vacuum deposition technique such as an evaporation method. The other is to bond a shield member made from a cap made of glass to the organic electroluminescent element.

[0014]

As the method for sealing the organic electroluminescent element by forming the protective film, for example, a method is disclosed in Japanese Published Patent Application No. H6-96858, by which  $\text{GeO}$ ,  $\text{SiO}$ ,  $\text{AlF}_3$ , or the like is deposited on an outer surface of the organic electroluminescent element by an ion plating method. In addition,  
5 a method is disclosed in Japanese Published Patent Application No. H7-211455, by which a protective film is formed from a water absorption substance with a water absorption rate of 1 % or more and a substance with moisture barrier properties of 0.1 % or less.

[0015]

As the method for sealing the organic electroluminescent element by bonding  
10 the shield member, there is a method in which a glass plate is provided on outer side of a backplane electrode, and a space between the backplane electrode and the glass plate is filled and sealed with **silicone oil** and the like, which has been already used for the inorganic electroluminescent element. In addition, a method is disclosed in Japanese Published Patent Application No. H5-089959, by which shielding is performed with  
15 electric insulation glass or electric insulating-airtight fluid after a protective film is formed of an insulating inorganic compound. In the case of the method for performing shielding with electric insulating-airtight fluid, a method is shown, in which a glass container or the like is filled and sealed with an inert gas, **silicon oil** or the like, and an opening is attached with an epoxy resin or the like.

20 [0016]

As a consequence of examination from various views about growth of the dark spot, the inventors of this invention found that even a little amount of moisture exiting in the vacuum of about  $10^{-4}$  Torr promotes growth of the dark spot.

[0017]

25 Generation of the dark spot is mainly caused by pollution on the anode of an ITO film or the like and dust attached to the substrate 1. In the case of the ITO film, pollution on its surface can be almost solved by devising a cleaning method. However, it is difficult to remove dust attached to the substrate 1 completely. For example, even when the organic electroluminescent element is manufactured in a clean room of class 100, dust  
30 with a particle diameter of about 3  $\mu\text{m}$  exits at a rate of one piece of dust/10 liter.

Furthermore, a large amount of dust exits in a vacuum deposition apparatus used through the manufacturing process, and dust is often attached to the substrate 1 in deposition. Accordingly, even if work is conducted in the clean room with high degree of cleanness, dust exits on the substrate 1 at a high rate, and it is extremely difficult to prevent  
5 generation of dark spot itself completely.

[0018]

The dark spot is caused by dust of about several  $\mu\text{m}$  exiting on the substrate 1. Dust cannot be completely covered with the organic thin film layer 3 of about  $0.1\ \mu\text{m}$ , the cathode 6 of about  $0.2\ \mu\text{m}$ , and the protective film of about  $0.5\ \mu\text{m}$ , which is formed  
10 thereover, as in the conventional organic electroluminescent element because the total thickness is about  $1\ \mu\text{m}$ . Accordingly, even if the protective film itself has properties that oxygen and moisture are not transmitted at all, when dust cannot be completely covered with the protective film, oxygen and moisture penetrate the organic thin film layer 3 and the cathode 6 from the periphery of the dust, and as a result, dark spot is made  
15 to grow.

[0019]

Accordingly, in order to prevent growth of the dark spot completely, it is necessary to block intrusion of moisture and oxygen into the materials used for the cathode 6 and the organic thin film layer 3 almost completely.

20 [0020]

Incidentally, as an organic material used in the organic electroluminescent element, a heating temperature that is allowable in the manufacturing process has an upper limit of about  $100\ ^\circ\text{C}$  in accordance with the characteristics thereof. In a case where the protective film is formed by an evaporation method or the like, the heating  
25 temperature cannot exceed this temperature. However, in a case of using oxide such as  $\text{GeO}$ ,  $\text{SiO}$ , or  $\text{SiO}_2$  used for the protective film, it is difficult to form a dense film sufficiently at a low temperature of about  $100\ ^\circ\text{C}$  in general. On such deposition conditions, a large number of defects and pinholes exit in the film, and moisture and oxygen cannot be completely blocked. Further, even if theses problems are tried to be  
30 improved by increasing the thickness, internal stress of the protective film is increased

with increase of the thickness, and the cathode 6 and the organic thin film layer 3 are damaged, so that there is a possibility in that emission luminance is reduced and the organic electroluminescent element is short-circuited.

[0021]

5 Further, the conventional sealing with the shield member which has been tried also has failed to reach the complete suppression of the growth of dark spots till now. An epoxy resin used for the bond of the electric insulating glass described in Japanese Published Patent Application No. H5-089959 described above and the substrate 1 has a transmitting property of moisture vapor of 3 to 5 ( $\text{g/m}^2 \cdot 24\text{h/mm}$ ), and a polyimide resin  
10 has a transmitting property of moisture vapor of 2 ( $\text{g/m}^2 \cdot 24\text{h/mm}$ ), whereby moisture intrusion from an adhesive portion cannot be completely suppressed.

[0022]

Thus, it has been impossible to suppress the growth of dark spots completely by bond with the protective film and the glass cap used for the conventional organic  
15 electroluminescent element.

[0023]

The present invention is to solve the above problem. It is a purpose to provide an organic electroluminescent element, a liquid crystal lighting system, a display device having excellent durability and reliability for securing long-term characteristics, and a  
20 method for manufacturing the organic electroluminescent element.

[0024]

[Means for solving the Problems]

In order to solve the above project, an organic electroluminescent element, a liquid crystal lighting system, and a display device of the invention are provided with a  
25 substrate; a stacked structure including an anode, an organic thin film layer, and a cathode stacked over the substrate; a shield member provided over the substrate to cover an outer surface side of the stacked structure; and an adhesive member provided between the substrate and the shield member. It is a feature that the adhesive member bonds the substrate and the shield member. In accordance with this structure, an organic  
30 electroluminescent element having excellent durability and reliability for securing

long-term characteristics and a display device using an organic electroluminescent element can be provided.

[0025]

A method for manufacturing an organic electroluminescent element of the invention includes a step of melting the adhesive member, and a step of bonding the substrate and the shield member using the melted adhesive member. In accordance with this structure, the organic electroluminescent element is locally heated, whereby bonding can be conducted without thermal destruction. Thus, an organic electroluminescent element with high reliability can be provided, and a method for manufacturing an organic electroluminescent element with excellent mass productivity can be provided.

[0026]

[Embodiment Mode of the Invention]

The invention described in the Claim 1 of the present invention is an organic electroluminescent element which includes a substrate, a stacked structure including an anode, an organic thin film layer, and a cathode stacked over the substrate, a shield member provided on the substrate to cover an outer surface side of the stacked structure, and an adhesive member provided between the substrate and the shield member. The organic electroluminescent element has a function of suppressing deterioration in characteristics accompanied with oxidization, swelling, and the like of the anode, the organic thin film layer, and the cathode by reducing the intrusion amount of moisture and oxygen from an external side.

[0027]

The invention described in Claim 2 of the present invention is the organic electroluminescent element described in Claim 1, characterized in that the anode, the organic thin film layer, and the cathode are stacked in this order on the substrate. The organic electroluminescent element has a function of suppressing deterioration in characteristics accompanied with oxidation, swelling, and the like of the anode, the organic thin film layer, and the cathode by reducing the intrusion amount of moisture and oxygen from an external side.

[0028]

The invention described in Claim 3 of the present invention is the organic electroluminescent element described in Claim 1 or 2, characterized in that a part of or the entire anode is made of a carbon thin film. The organic electroluminescent element has a function of enhancing adhesion of a carbon thin film as the anode and the organic thin film layer.

[0029]

The invention described in Claim 4 of the present invention is the organic electroluminescent element described in Claim 1, characterized in that the stacked structure is formed by stacking the anode, a carbon thin film, the organic thin film layer, and the cathode in this order on the substrate. The organic electroluminescent element has a function of enhancing adhesion of the anode and the organic thin film layer through the carbon thin film.

[0030]

The invention described in Claim 5 of the present invention is the organic electroluminescent element described in Claim 1, characterized in that the anode, a carbon thin film, the organic thin film layer, and the cathode are stacked in this order on the substrate. The organic electroluminescent element has a function of enhancing adhesion of the anode and the organic thin film layer through the carbon thin film.

[0031]

The invention described in Claim 6 of the present invention is the organic electroluminescent element described in any one of Claims 1 to 5, characterized in that at least a part of the adhesive member bonds the substrate and the shield member. The organic electroluminescent element has a function of suppressing deterioration in characteristics accompanied with oxidation, swelling, and the like of the anode, the organic thin film layer, and the cathode by reducing the intrusion amount of moisture and oxygen from an external side.

[0032]

The invention described in Claim 7 of the present invention is the organic electroluminescent element described in any one of Claims 1 to 6, characterized in that the organic thin film layer emits light when voltage is applied to the anode and the

cathode. The organic electroluminescent element has a function as a light-emitting layer.

[0033]

The invention described in Claim 8 of the present invention is the organic electroluminescent element described in any one of Claims 1 to 7, characterized in that the substrate is made of any one of a transparent substrate and a semi-transparent substrate. The organic electroluminescent element has a function as an element for a liquid crystal lighting system or a display device by conducting light emission to an external side.

10 [0034]

The invention described in Claim 9 of the present invention is the organic electroluminescent element described in any one of Claims 1 to 8, characterized in that the adhesive member is made from any one of low-melting point glass, a low-melting solder, and liquid crystal polymer. The organic electroluminescent element has a function of bonding the substrate and the shield member at a low temperature without destruction of the organic thin film layer.

[0035]

The invention described in Claim 10 of the present invention is the organic electroluminescent element described in any one of Claims 1 to 9, characterized in that the adhesive member has a melting point of 500 °C or lower. The organic electroluminescent element has a function of bonding the substrate and the shield member at a low temperature without destruction of the organic thin film layer.

[0036]

The invention described in Claim 11 of the present invention is the organic electroluminescent element described in Claim 9, characterized in that the low-melting glass is made of any one of low-melting glass of a Pb-B-Sn-Si-Al-O compound, a Sn-Pb-O-F compound, a Pb-Sn-P-O-Cl compound, and a PbO-SnO-P<sub>2</sub>O<sub>5</sub> compound. The organic electroluminescent element has a function of bonding the substrate and the shield member at a low temperature without destruction of the organic thin film layer.

30 [0037]

The invention described in Claim 12 of the present invention is the organic electroluminescent element described in any one of Claims 1 to 11, characterized in that the shield member is formed from any one of electric insulating glass and stainless steel. The organic electroluminescent element has a function of suppressing deterioration in characteristics accompanied with oxidation, swelling, and the like of the anode, the organic thin film layer, and the cathode by reducing the intrusion amount of moisture and oxygen from an external side, and of preventing breakdown and corrosion of the organic electroluminescent element due to external force by mechanical strength and corrosion resistance thereof.

10 [0038]

The invention described in Claim 13 of the present invention is the organic electroluminescent element described in Claim 12, characterized in that the shield member has a cap shape. The organic electroluminescent element has a function of protecting the organic thin film layer from external force without destruction of the organic thin film layer by providing a space which houses the organic thin film layer.

15 [0039]

The invention described in Claim 14 of the present invention is the organic electroluminescent element described in any one of Claims 1 to 13, characterized in that a protective film is provided to cover the stacked structure between the stacked structure and the shield member. The organic electroluminescent element has a function of preventing oxidation, swelling, and the like of the anode, the organic thin film layer, and the cathode even when moisture and oxygen penetrate from an external side, of suppressing deterioration in characteristics accompanied therewith.

[0040]

25 The invention described in Claim 15 of the present invention is the organic electroluminescent element described in Claim 14, characterized in that the adhesive member is made of a low-melting solder; and the protective film is an electric insulating compound layer and electrically separates the anode and the cathode. The organic electroluminescent element has a function of reducing the intrusion amount of moisture and oxygen from an external side; of suppressing deterioration in characteristics

30



accompanied with oxidation, swelling, and the like of the anode, the organic thin film layer, and the cathode even when moisture and oxygen penetrate from an external side; and of preventing the short circuit of the anode and the cathode by interposing a conductive solder therebetween.

5 [0041]

The invention described in Claim 16 of the present invention is the organic electroluminescent element described in Claim 14, characterized in that a film thickness of the protective film is 3  $\mu\text{m}$  to 30  $\mu\text{m}$ . The organic electroluminescent element has a function of preventing oxidation, swelling, and the like of the anode, the organic thin film  
10 layer, and the cathode even when moisture and oxygen penetrate from an external side, and of suppressing deterioration in characteristics accompanied therewith.

[0042]

The invention described in Claim 17 of the present invention is the organic electroluminescent element described in Claim 14, characterized in that the protective  
15 film is a stacked film of at least two or more layers which have an insulating compound layer in the lowest layer and a metal layer in the top layer. The organic electroluminescent element has a function of preventing oxidation, swelling, and the like of the anode, the organic thin film layer, and the cathode even when moisture and oxygen penetrate from an external side, and of suppressing deterioration in characteristics  
20 accompanied therewith; and of conducting and heating heat by the metal layer in the top layer, so that deterioration in characteristics due to heat of the organic thin film layer can be reduced.

[0043]

The invention described in Claim 18 of the present invention is the organic  
25 electroluminescent element described in any one of Claims 1 to 17, characterized in that an electric insulating buffer layer is provided on an adhesive surface of at least one of the substrate and the shield member. The organic electroluminescent element has a function of enhancing adhesive strength between the substrate and the shield member by the electric insulating buffer layer; and of suppressing deterioration in characteristics  
30 accompanied with oxidation, swelling, and the like of the anode, the organic thin film

layer, and the cathode by reducing the intrusion amount of moisture and oxygen from an external side.

[0044]

The invention described in Claim 19 of the present invention is the organic  
5 electroluminescent element described in Claim 18, characterized in that the electric  
insulating buffer layer is any one of  $\text{SiO}_2$  and  $\text{SiO}$ . The organic electroluminescent  
element has a function of enhancing adhesive strength between the substrate and the  
shield member by the electric insulating buffer layer; and of suppressing deterioration in  
characteristics accompanied with oxidation, swelling, and the like of the anode, the  
10 organic thin film layer, and the cathode by reducing the intrusion amount of moisture and  
oxygen from an external side.

[0045]

The invention described in Claim 20 of the present invention is the organic  
electroluminescent element described in any one of Claims 1 to 19, characterized in that  
15 the cathode is made of any one of an Al based alloy containing Mg, an Al based alloy  
containing Mg and Li, an Al based alloy containing Mn, and an Al based alloy containing  
Mn and Li. The organic electroluminescent element has a function of improving  
corrosion resistance of the cathode and of enhancing reliability.

[0046]

20 The invention described in Claim 21 of the present invention is an organic  
electroluminescent element component characterized by including the organic  
electroluminescent element described in any one of Claims 1 to 20, an electrode driver IC  
provided on the substrate in order to drive the anode and the cathode, and a leading line  
provided on the substrate in order to connect the electrode driver IC, which has a function  
25 as a component of a liquid crystal lighting system and a display device.

[0047]

The invention described in Claim 22 of the present invention is the organic  
electroluminescent element component described in Claim 21, characterized in that the  
leading line has a stacked structure; and conductivity of an upper layer is higher than that  
30 of a lower layer. The organic electroluminescent element component has a function of

conducting voltage applied to the leading line effectively to the anode and the cathode, whereby the light-emitting layer can be driven.

[0048]

The invention described in Claim 23 of the present invention is the organic electroluminescent element component described in Claim 21 or 22, characterized in that the cathode has a stacked structure; and conductivity of an upper layer is higher than that of a lower layer. The organic electroluminescent element component has a function of conducting voltage applied to the cathode effectively to the light-emitting layer.

[0049]

The invention described in Claim 24 of the present invention is a liquid crystal lighting system characterized by including the organic electroluminescent element described in any one of Claims 1 to 20, means for driving the anode and the cathode, and a liquid crystal panel provided on a front side of the organic electroluminescent element, in which lighting is conducted by applying voltage to the organic electroluminescent element. The liquid crystal lighting system has a function of small deterioration in characteristics with time, and excellent reliability.

[0050]

The invention described in Claim 25 of the present invention is a display device characterized by including the organic electroluminescent element described in any one of Claims 1 to 20, means for driving the anode and the cathode, and a liquid crystal panel provided on a front side of the organic electroluminescent element, in which display function is performed by applying matrix voltage to the organic electroluminescent element. The display device has a function of small deterioration in characteristics with time, and excellent reliability.

[0051]

The invention described in Claim 26 of the present invention is a method for manufacturing an organic electroluminescent element characterized by including a step of forming a stacked structure by stacking an anode, an organic thin film layer, and a cathode on a substrate; a step of providing a shield member to cover an outer surface side of the stacked structure through an adhesive member on the substrate; a step of melting

the adhesive member; and a step of bonding the substrate and the shield member with the melted adhesive member. The method for manufacturing an organic electroluminescent element has a function of providing an organic electroluminescent element with small deterioration in characteristics with time and excellent reliability.

5 [0052]

The invention described in Claim 27 of the present invention is the method for manufacturing an organic electroluminescent element described in Claim 26, characterized in that the step of forming a stacked structure is a step of stacking an anode, a carbon thin film, an organic thin film layer, and a cathode on a substrate. The method  
10 for manufacturing an organic electroluminescent element has a function of suppressing deterioration in characteristics accompanied with oxidation, swelling, and the like of the anode, the organic thin film layer, and the cathode by reducing the intrusion amount of moisture and oxygen from an external side.

[0053]

15 The invention described in Claim 28 of the present invention is the method for manufacturing an organic electroluminescent element described in Claim 26 or 27, characterized in that the substrate is a transparent or semi-transparent substrate. The method for manufacturing an organic electroluminescent element has a function of conducting light emission to an external side, and of providing an element for a liquid  
20 crystal lighting system and a display device.

[0054]

The invention described in Claim 29 of the present invention is the method for manufacturing an organic electroluminescent element described in any one of Claims 26 to 28, characterized in that the adhesive member is made from any one of low-melting  
25 glass, a low-melting solder, and liquid crystal polymer. The method for manufacturing an organic electroluminescent element has a function of bonding the substrate and the shield member at a low temperature without destruction of the organic thin film layer.

[0055]

The invention described in Claim 30 of the present invention is the method for  
30 manufacturing an organic electroluminescent element described in any one of Claims 26

to 29, characterized in that the step of melting an adhesive member is a step of melting the adhesive member using laser process or a step of melting the adhesive member using an ultrasonic wave. The method for manufacturing an organic electroluminescent element has a function of suppressing rise in temperature of the stacked structure because a bonding part of the substrate and the shield member is locally heated, whereby an organic electroluminescent element with an excellent light-emitting characteristic and excellent reliability can be provided by blocking moisture and oxygen from an external side.

[0056]

(Embodiment Mode 1)

Embodiment modes of the present invention are described below with drawings.

[0057]

FIG. 1 is a cross-sectional view of an essential part of an organic electroluminescent element in one embodiment mode of the invention.

[0058]

A substrate 1 is made of transparent or semi-transparent glass, PET (polyethylene terephthalate), polycarbonate, amorphous polyolefin, or the like. The substrate 1 may be also a flexible substrate 1 having flexibility in a thin film of such materials.

[0059]

An anode 2 is formed of ITO, ATO ( $\text{SnO}_2$  doped with Sb), AZO (ZnO doped with Al), and the like.

[0060]

An organic thin film layer 3 may be a single layer structure of a light-emitting layer 5 only; a two-layer structure of a hole transporting layer 4 and the light-emitting layer 5, or the light-emitting layer 5 and an electron transporting layer (not shown); or a three-layer structure of the hole transporting layer 4, the light-emitting layer 5, and the electron transporting layer. In the case of such a two-layer structure or three-layer structure, however, the hole transporting layer 4 and the anode 2, or the electron transporting layer and a cathode 6 are stacked so as to be contacted with each other.

[0061]

The light-emitting layer 5 is preferred to have a fluorescent characteristic in the visible region, being made of a fluorescent material of excellent film forming property, of which examples include, aside from Alq<sub>3</sub> and Be-benzoquinolinol (BeBq<sub>2</sub>),

2,5-bis(5,7-di-*t*-pentyl-2-benzoxazolyl)-1,3,4-thiadiazole,

5 4,4'-bis(5,7-benzyl-2-benzoxazolyl)stilbene,

4,4'-bis[5,7-di-(2-methyl-2-butyl)-2-benzoxazolyl]stilbene,

2,5-bis(5,7-di-*t*-benzyl-2-benzoxazolyl)thiophene,

2,5-bis([5- $\alpha$ , $\alpha$ -dimethylbenzyl]-2-benzoxazolyl)thiophene,

2,5-bis[5,7-di-(2-methyl-2-butyl)-2-benzoxazolyl]-3,4-diphenylthiophene,

10 2,5-bis(5-methyl-2-benzoxazolyl)thiophene, 4,4'-bis(2-benzoxazolyl)biphenyl,

5-methyl-2-[2-[4-(5-methyl-2-benzoxazolyl)phenyl]vinyl]benzoxazolyl,

2-[2-(4-chlorophenyl)vinyl]naphtho[1,2-d]oxazole, other benzoxazole system,

2,2'-(*p*-phenylenedivinylene)bisbenzothiazole, other benzothiazole system,

2-[2-[4-(2-benzimidazolyl)phenyl]vinyl]benzimidazole,

15 2-[2-(4-carboxyphenyl)vinyl]benzimidazole, other fluorescence brightener of other benzimidazole system, tris(8-quinolinol)aluminum, bis(8-quinolinol)magnesium,

bis(benzo[f]-8-quinolinol)zinc, bis(2-methyl-8-quinolinolate)aluminumoxide,

tris(8-quinolinol)indium, tris(5-methyl-8-quinolinol)aluminum, 8-quinolinol lithium,

tris(5-chloro-8-quinolinol)gallium, bis(5-chloro-8-quinolinol)calcium,

20 poly[zinc-bis(8-hydroxy-5-quinolinol)methane], other 8-hydroxy quinoline metal complex, dilithium epindridion, other metal chelate oxide compound,

1,4-bis(2-methylstyryl)benzene, 1,4-(3-methylstyryl)benzene,

1,4-bis(4-methylstyryl)benzene, distyryl benzene, 1,4-bis(2-ethylstyryl)benzene,

1,4-bis(3-ethylstyryl)benzene, 1,4-bis(2-methylstyryl)-2-methyl benzene, other styryl

25 benzene compound, 2,5-bis(4-methylstyryl)pyrazine, 2,5-bis(4-ethylstyryl)pyrazine,

2,5-bis[2-(1-naphthyl)vinyl]pyrazine, 2,5-bis(4-methoxystyryl)pyrazine,

2,5-bis[2-(4-biphenyl)vinyl]pyrazine, 2,5-bis[2-(1-pyrenyl)vinyl]pyrazine, other distyl pyrazine derivative, naphthalimide derivative, perylene derivative, oxadiazole derivative, aldazine derivative, cyclopentane diene derivative, styryl amine derivative, coumarin

30 derivative, and aromatic dimethyldine derivative. Further, anthracene, salicylate,

pyrene, coronen, and the like, may be also used.

[0062]

A material for the hole transporting layer 4 is preferably high in hole mobility, transparent, and excellent in film forming property, which may include, aside from  
 5 trphenylamine derivative like TPD, porphin, tetraphenyl porphin copper, phthalocyanine, copper phthalocyanine, titanium phthalocyanine oxide, other porphyrin compound, 1,1-bis{4-(di-*P*-trylamino)phenyl}cyclohexane, 4,4',4"-trimethyl triphenyl amine, *N,N,N,N*-tetraxis(*P*-tolyl)-*P*-phenylenediamine, 1-(*N,N*-di-*P*-tolylamino)naphthalene, 4,4'-bis(dimethylamino)-2,2'-dimethyl triphenyl methane,  
 10 *N,N,N,N*-tetraphenyl-4,4'-diaminobiphenyl, *N,N*-diphenyl-*N,N*-di-*m*-tolyl-4, *N,N*-diphenyl-*N,N*-bis(3-methylphenyl)-1,1'-4,4'-diamine, 4'-diaminobiphenyl, *N*-phenyl carbazole, other aromatic tertiary amine, 4-di-*P*-tolylamino stilbene, 4-(di-*P*-tolylamino)-4'-[4-(di-*P*-tolylamino)styryl]stilbene, other stilbene compound, triazole derivative, oxadiazole derivative, imidazole derivative, polyaryl alkane  
 15 derivative, pyrazoline derivative, pyrazolone derivative, phenylene diamine derivative, anylamine derivative, amino substituent chalcone derivative, oxazole derivative, styryl anthracene derivative, fluorenone derivative, pydrazone derivative, silazane derivative, polysilane aniline copolymer, high polymer oligomer, styryl amine compound, aromatic dimethylidene compound, poly-3-methyl dimophene and other organic material. Also, a  
 20 high polymer dispersion system of an organic material for hole transporting layer 4 of low molecular weight dispersed in high polymer of polycarbonate or the like may be used as the hole transporting layer 4.

[0063]

A material for the electron transporting layer includes 1,3-bis(4-*tert*-butyl  
 25 phenyl-1,3,4-oxadiazolyl)phenylene (OXD-7), other dioxadiazole derivative, anthraquinone dimethane derivative, diphenyl quinone derivative, and others.

[0064]

The cathode 6 is composed of Al, In, Mg, Ti, another metal, a Mg-Ag alloy, a Mg-In alloy, other Mg alloy, an Al-Li alloy, an Al-Sr alloy, an Al-Ba alloy, other Al alloy,  
 30 and others. In particular, the Al-Mg alloy or the Al-Li-Mg alloy which is one of the

present invention is a metal with low work function and excellent corrosion resistance, which is particularly effective.

[0065]

Further, a conductive layer with high conductivity may be stacked over the cathode 6. At this time, the conductive layer is formed of any one kind of copper, silver, gold, aluminum, iron, nickel, molybdenum, and platinum, an alloy thereof, or an alloy containing these metals; and has a function in which electric resistance of the cathode is reduced, and variation in emission luminance due to difference in current values of each cathode can be prevented.

10 [0066]

As a protective film 7, an insulating compound layer is used, for example, GeO, SiO, SiO<sub>2</sub>, MoO<sub>3</sub>, other oxide, AlN, Si<sub>3</sub>N<sub>4</sub>, other nitride, PET, or other thermoplastic organic high polymer, and GeO is particularly preferred.

[0067]

15 It is one of the features of the invention that a shield member 8 of stainless steel, glass, or the like is used and is bonded to the substrate 1 with an adhesive layer 9 of low-melting glass, a low-melting solder, liquid crystal polymer, or the like to seal the organic thin film EL element. Examples of the low-melting glass include Pb-B-Sn-Si-Al-O system T187 and Sn-P-Pb-O-F system low-melting glass, 20 Pb-Sn-P-O-Cl system low-melting glass (L. Hu & Z. Jiamg Phys. Chem. Glasses 35 (1993) 38), and PbO-SnO-P<sub>2</sub>O<sub>5</sub> system low melting glass. As the low-melting solder, a solder whose melting point is 500 °C or less, and a tin-lead alloy, a tin-antimony alloy, a bismuth alloy, or the like is used. In particular, as a tin-lead alloy, Serasolza manufactured by Asahi Glass CO., LTD (No. 123, No. 143, No. 186, No. 224, No. 246) is 25 preferably used. Furthermore, the shield member 8 and the substrate 1 on which the organic electroluminescent element is formed may be directly bonded with low melting glass, or in order to improve further the wettability with the low melting glass, for example, a buffer layer of SiO<sub>2</sub>, SiO or the like may be formed in at least one of substrate 1 and shield member 8.

30 [0068]



As the adhesion between the shield member 8 and the substrate 1, nearly same effects are confirmed by using, aside from low-melting glass and low-melting solder, liquid crystal polymer having a far excellent moisture resistance as compared with an epoxy resin, a polyimide resin, and other high polymer adhesives. The liquid crystal polymer used in the invention is a rigid high polymer in a rod shape, mostly having a skeleton of aromatic polyester, but also amide bond or ether bond may be included. The detail is described in a feature article in "High Polymer", October 1994, edited by Japan Society of High Polymer. The liquid crystal high polymer is hardly changed in structure when solidified, and is known for merits such as fast solidifying speed, small shrinkage, and high gas barrier performance, and is initially developed by Carborundum Company, Eastman Kodak Company, Hoechst Celanese Corporation and others, and is distributed by many manufacturers in the trade-names of Bectran, Rodran, Zider, etc. These products are, however, only in the initial stage of application in injection molding, textile, and film, and nothing has been specifically studied for use in resin adhesive for sealing the organic electroluminescence as in the invention, and optimum method of use and effects could not be predicted. The inventors accumulated intensive studies, and obtained effects more than expected beyond the performance of the conventional resin when used as sealing resin of organic electroluminescence.

[0069]

The structure of the organic electroluminescent element manufactured by the invention is not particularly defined, and aside from the structure of anode 2/hole transporting layer 4/light-emitting layer 5/cathode 6 mentioned above, other structures are possible, for example, a single layer type element of anode 2/light-emitting layer 5/cathode 6, two-layer structure of anode 2/light-emitting layer 5/electron transporting layer/cathode 6, and three-layer structure of anode 2/hole transporting layer 4/light-emitting layer 5/electron transporting layer/cathode 6.

[0070]

The reliability may be further improved by controlling the film thickness of the insulating compound layer 7 as the protective film, in particular, by stacking a metal conductive film on the insulating compound layer 7.

[0071]

Next, a method for manufacturing an organic electroluminescent element of the invention is described below.

[0072]

5 First, by a known method, the anode 2 formed of ITO or the like, the hole transporting layer 4 formed of TPD or the like, the light-emitting layer 5 formed of Alq<sub>3</sub> or the like, and the cathode formed of an Al-Li alloy or the like are sequentially stacked on the substrate such as glass by a resistance heating deposition method, an ion beam sputtering method, or the like. The insulating compound layer 7 formed of GeO or the  
10 like may be formed on the cathode 6.

[0073]

Next, as an adhesive step, the shield member 8 is bonded to the substrate 1 with the low-melting glass or the low-melting solder.

[0074]

15 A method using laser light or an ultrasonic wave is given as a method for bond of the shield member 8 with the low-melting glass or the low-melting solder.

[0075]

In the case of a method using laser light, after the shield member 8 to which the low-melting glass, the low-melting solder, or the liquid crystal polymer is attached is set  
20 at a predetermined portion on the substrate 1, the low-melting glass or low-melting solder portion or an adhesive portion of the shield member 8 or the substrate 1 is irradiated with laser light again, and the low-melting glass or the low-melting solder is melted, so that the substrate 1 and the shield member 8 are bonded with each other.

[0076]

25 In the case of a method using an ultrasonic soldering apparatus, first, the low-melting solder is melted by the ultrasonic soldering apparatus and attached to the adhesion portion of the shield member 8 and the substrate 1, and the shield member 8 is set at a predetermined portion on the substrate 1; thereafter, the low-melting solder portion is melted again by the ultrasonic soldering apparatus, so that the substrate 1 and  
30 the shield member 8 are bonded with each other.

[0077]

When the ultrasonic wave and laser light is used, a heating temperature can be suppressed to be low, and the adhesion portion can be limited locally as well as the substrate 1 and the shield member 8 can be bonded in extremely short time period, so that  
5 destruction of the organic electroluminescent element can be prevented.

[0078]

Next, a further specific structure of Embodiment Mode 1 is shown. First, in order to form a specified pattern shape on a glass substrate 1 on which an ITO film is formed entirely, the ITO film 2 (film thickness 160 nm) is etched by using hydrochloric acid. This substrate 1 is cleaned ultrasonically for 5 minutes with a detergent (Semico  
10 Clean, manufactured by Furuuchi Chemical Corporation), further cleaned ultrasonically for 10 minutes in purified water, and cleaned ultrasonically for 5 minutes in a solution of ammonia and hydrogen peroxide (1:1:5), finally cleaned ultrasonically for 5 minutes in purified water at a temperature of 70 °C, water is blown away by nitrogen blower, and  
15 then it is heated and dried at a temperature of 250 °C. Thus cleaned substrate 1 is set in a resistance heating deposition apparatus, the chamber is evacuated to a degree of vacuum of  $2 \times 10^{-6}$  Torr or less, and a hole transporting layer 4 of about 500 Å is formed by using TPD as an evaporation source. In succession, using  $\text{Alq}_3$  as an evaporation source, a light-emitting layer 5 of about 750 Å is formed. The deposition speed is not particularly  
20 defined, but it was performed at 2 Å/s in both operations. Next, in the same vacuum layer, using an AlLi alloy containing 15 at % of Li as an evaporation source, a cathode 6 is formed in a film thickness of 2000 Å. Further, using GeO as an evaporation source, a protective layer 7 is formed in a film thickness of 3000 Å. The substrate 1 on which this element was formed was taken out of the vacuum chamber, and a shield member 8 was  
25 formed outside of the element in the following procedure. Using SUS303 (Fe-Cr-Ni alloy) as the shield member 8, first, low-melting glass was applied on the portion contacting with the substrate 1. The low melting glass was trade-name T187 manufactured by Iwaki Glass Co., Ltd., and after adjusting to the particle size of 300 meshes (43 µm or less), it was mixed with an organic binder having 1% of nitrocellulose  
30 blended in isoamyl acetate at a concentration ratio of 12 (low-melting glass) to 1 (organic

binder) by weight, and the mixture was applied on the adhesion area by using a brush. After application, in order to vaporize the solvent in the organic binder, it was dried for about 10 minutes at a temperature of 110 °C. In succession, this seal material was heated for 15 minutes in an electric furnace at 450 °C to melt the low-melting glass, and it was  
5 taken out, and is overlaid on the glass substrate 1 on which the element was formed, and sealing was completed. Incidentally, when bonding the glass substrate 1 and shield member 8, it was performed on a copper plate of high thermal conductivity so that the temperature of the element might not be elevated, and the temperature rise of the element was suppressed. In this way, an organic electroluminescent element bonded with the  
10 shield member 8 by low-melting glass was obtained.

[0079]

(Embodiment Mode 2)

First, in the same manner as in Embodiment Mode 1, an organic electroluminescent element is manufactured up to the process before bonding of the  
15 shield member 8. Then, low-melting glass of Sn-P-Pb-O-F system (Shoei Chemical Industries) ground to powder of 10 μm or less is mixed with methyl alcohol at a concentration ratio of 1:1 by weight to form a paste, which is applied on a white sheet glass of 1 mm in thickness manufactured by HOYA Corporation to be used as the shield member 8. In this white sheet glass, the portion confronting the forming portion of an  
20 organic electroluminescent element was drilled by 0.3 mm by a sand blasting method. This can prevent breakage due to contact of the shield glass with the organic electroluminescence element. Instead of a sand blasting method, a honing method may be also employed. Next, in order to vaporize the organic solvent, after once drying for 10 minutes at 100 °C, it is then heated for 10 minutes in an electric furnace at 300 °C, and  
25 taken out and overlaid and bonded to the glass substrate 1 on which the element is formed. By this method, the organic electroluminescent element using glass in the shield member 8 can be completed. The melting point of the low-melting glass used herein is 270 °C, but glass of any arbitrary melting point may be obtained by adjusting the composition.

[0080]

30 (Embodiment mode 3)

FIG. 6 is a structural view showing a manufacturing method in which the adhesive layer is bonded using a laser. This embodiment mode shows an example of weld using a YAG laser. After forming the element in the same manner as in Embodiment Mode 1, a low-melting glass 9 such as Sn-P-Pb-O-F system or the like is applied on a white sheet glass as a shield member 8 in the same manner as shown in Embodiment Mode 1. The light emitted from a YAG laser 13 (model ML-2330A manufactured by Miyachi Technos Corporation) is refracted by a reflection mirror 14 and entered into a lens 15. The light condensed by the lens 15 is applied from outside the shield member 8 while moving the element by an X-Y table, and the low-melting glass is melted and bonded. In the case of bonding the adhesive layer with a laser, an adhesive surface between the substrate and the shield member is necessary to be heated up to an equivalent temperature with a melting point of the adhesive member, while the organic thin film layer is easily damaged due to heat. According to the present invention, this adhesive surface can be locally heated, whereby the substrate and the shield member can be surly bonded without destruction of the organic thin film layer. The inventors found that when the melting point of the adhesive member and an operation temperature as a local temperature are 500 °C or less, the substrate and the shield member can be bonded without damaging an organic thin film layer used in this embodiment mode.

[0081]

In this embodiment, an example of using a YAG laser is presented, but other CO<sub>2</sub> laser or excimer laser may be also used. What is important is that the wavelength of each laser induces absorption with the shield substrate 1 or the low-melting glass to melt the low-melting glass, and the material for the substrate 1, shield member 8, low-melting glass, and laser may be selected. For example, when the low-melting glass absorbs the laser wavelength, the low-melting glass itself is melted, and when the shield member 8 absorbs the laser wavelength, the shield member 8 is warmed, and its heat is transmitted to the low-melting glass to be melted, or when the substrate 1 on which the element is formed absorbs the laser wavelength, it is warmed, and its heat is transmitted to the low-melting glass to be melted. Therefore, there is no particular limitation among the laser, low-melting glass, substrate 1, and shield member 8.

[0082]

(Embodiment Mode 4)

After forming an ITO film of 160 nm in film thickness on a glass substrate 1 by a sputtering method, a resist material (OFPR-800 manufactured by Tokyo Oka Co., Ltd) was applied on the ITO film by a spin coating method, and a resist film of 10  $\mu$ m in thickness was formed, and the resist film was patterned to a specified shape by masking, exposing and developing. This glass substrate 1 was immersed in 50% hydrochloric acid at 60 °C, and the ITO film in the portion free from the resist film was etched, and then the resist film was also removed, thereby obtaining a glass substrate 1 on which an anode 2 made of an ITO film of specified pattern was formed.

[0083]

This glass substrate 1 was cleaned ultrasonically for 5 minutes with a detergent (Semico Clean, manufactured by Furuuchi Chemical Corporation), cleaned ultrasonically for 10 minutes in purified water, cleaned ultrasonically for 5 minutes in a solution of 1 part (by volume) of ammonia water containing 1 part of hydrogen peroxide water and 5 parts of water, and cleaned ultrasonically for 5 minutes in purified water at 70 °C, sequentially, and moisture deposited on the glass substrate 1 was removed by nitrogen blower, and it was heated at 250 °C and dried.

[0084]

On the anode 2 side surface of the dried glass substrate 1, TPD was formed in a film thickness of about 50 nm as a hole transporting layer 4 in a resistance heating deposition apparatus evacuated to a degree of vacuum of  $2 \times 10^{-6}$  Torr or less.

[0085]

Next, similarly in the resistance heating deposition apparatus, Alq<sub>3</sub> was formed in a film thickness of about 75 nm as a light-emitting layer 5 on the hole transporting layer 4. The deposition speed of both TPD and Alq<sub>3</sub> was 0.2 nm/s.

[0086]

Also in the resistance heating deposition apparatus, a cathode 6 was formed in a film thickness of 200 nm on the light-emitting layer 5, using an Al-Li alloy containing 15 at % of Li as an evaporation source.

[0087]

In the resistance heating deposition apparatus, an insulating compound layer 7 was formed in a film thickness of about 3  $\mu\text{m}$  on the cathode 6, using  $\text{GeO}$  as an evaporation source.

5 [0088]

The glass substrate 1 on which the insulating compound layer 7 was formed was taken out of the deposition apparatus, and in the adhesive portion of the shield member 8 made of white sheet glass (1 mm thick, manufactured by HOYA Corporation) with the glass substrate 1, a low-melting solder (Serasolza No. 123, manufactured by Asahi Glass Co., Ltd) was applied by using an ultrasonic soldering apparatus (Sun Bonder USM-IV, manufactured by Asahi Glass Co., Ltd) in the condition of frequency of 50 kHz and heating temperature of 150  $^{\circ}\text{C}$ . After that, the shield member 8 is set on the glass substrate 1, the low-melting solder deposited on the white sheet glass was melted again by the ultrasonic soldering apparatus in the condition of frequency of 50 kHz, heating temperature of 150  $^{\circ}\text{C}$ , and vibrating time of 20 to 30 seconds, and then the glass substrate 1 and shield member 8 were bonded tightly.

[0089]

According to the above method, an organic electroluminescent element was manufactured, which was presented as Embodiment Mode 4.

20 [0090]

(Embodiment Mode 5)

Same as in Embodiment Mode 1, a glass substrate 1 was manufactured by stacking an anode 2 made of an ITO film, a hole transporting layer 4 made of TPD, a light-emitting layer 5 made of  $\text{Alq}_3$ , a cathode 6 made of an Al-Li alloy, and an insulating compound layer 7 made of  $\text{GeO}$  thereon.

[0091]

The glass substrate 1 on which the insulating compound layer 7 was formed was taken out of the deposition apparatus, and in the adhesive portion of a shield member 8 made of white sheet glass (1 mm thick, manufactured by HOYA Corporation) forming a depression with depth of 0.3 mm in the central part by a sand blasting method, with the

glass substrate 1, a low-melting solder (Serasolza No. 246, manufactured by Asahi Glass Co., Ltd) was applied by using an ultrasonic soldering apparatus (Sun Bonder USM-IV, manufactured by Asahi Glass Co., Ltd), in the conditions of frequency of 50 kHz and heating temperature of 250 °C. After that, the shield member 8 was fixed on the glass substrate 1, and the low-melting solder deposited on the white sheet glass was irradiated with laser light by using a YAG laser irradiation apparatus (ML-2330A, manufactured by Miyachi Technos Corporation) to melt the low-melting solder, and then the glass substrate 1 and the shield member 8 were bonded.

[0092]

According to the above method, an organic electroluminescent element same as in Embodiment Mode 1 was manufactured, which was presented as Embodiment Mode 5.

[0093]

(Comparative Example 1)

In order to confirm the effect of the organic electroluminescence elements of the invention presented in Embodiment Modes 1, 2, 3, 4, 5, a conventional organic electroluminescent element was manufactured by using an epoxy resin in adhesion between the shield member 8 and glass substrate 1, and growth of dark spots was compared. The epoxy resin used in the conventional organic electroluminescent element was composed of ECR-7125 used as main agent and ECH-7125 as hardener (both manufactured by Sumitomo Bakelite Co., Ltd), blended at a ratio of 10:6, which was cured for 12 hours at 50 °C. The shield member 8 was the same white sheet glass manufactured by HOYA Corporation as used in Embodiment Mode 1. The organic electroluminescent element for comparison was same in all of the material, composition, and film forming condition, except for the resin used for adhesion. These three elements were stored in an environmental cell at 60 °C and 95%, and growth of dark spots was observed.

[0094]

In order to investigate changes with time of dark spots in three organic electroluminescence elements of Embodiment Modes 1 and 2 and Comparative Example 1, each was stored in a thermostatic cell controlled at 60 °C and 95% of humidity, and the



mean diameter of dark spot was microscopically observed at specific time intervals. The result is explained by referring to FIG. 7. FIG. 7 is a relation diagram of storage time and growth of the dark spots in embodiment modes of the invention. As clear from FIG. 7, in the examples of the invention using low-melting glass in adhesion of the shield member 8, growth of dark spots was notably suppressed as compared with the conventional organic electroluminescent element using an epoxy resin in adhesion. According to the invention using low-melting glass as adhesive, a longer life time of organic electroluminescent element may be achieved.

[0095]

The organic electroluminescent element is not highly resistant to heat, and hence the low-melting glass used for adhesion is required to be melted at low temperature. Accordingly, the working temperature for melting the glass is preferred to be 500 °C or less owing to the characteristic of the organic electroluminescence element. However, the material is not particularly defined, and any material may be used as far as the moisture resistance is better than that of organic resin.

[0096]

In order to investigate changes with time of dark spots in three organic electroluminescence elements of Embodiment Modes 4 and 5 and Comparative Example 1, each was stored in a thermostatic cell controlled at 60 °C and 95% of humidity, and the mean diameter of dark spot was microscopically observed at specific time intervals. The result is shown in FIG. 8.

[0097]

FIG. 8 is a relation diagram of storage time and mean diameter of dark spots. As clear from FIG. 8, in the organic electroluminescent element of Comparative Example 1, the mean diameter of dark spots increases along with the passing of the storage time, whereas in the organic electroluminescence elements of Embodiment Modes 4 and 5, notable changes in mean diameter of dark spots were not recognized in spite of very severe environments of 60 °C and humidity of 95% for the organic electroluminescence element, and it was found that growth of dark spots was prevented. In particular, in the organic electroluminescent element of Embodiment 1, it was clear that growth of dark

spots was prevented nearly perfectly.

[0098]

(Embodiment Mode 6)

FIG. 2 is a cross-sectional view of an essential part of an organic  
5 electroluminescent element in one embodiment mode of the invention.

[0099]

In FIG. 2, reference numeral 7 denotes a protective film; 7a, a lowest layer; 7b,  
an upper layer; 8, a glass cap; and 9, an adhesive layer. A substrate 1, an anode 2, an  
organic thin film layer 3, a hole transporting layer 4, a light-emitting layer 5, and a  
10 cathode 6 are similar to the mentioned above.

[0100]

The organic electroluminescent element in this embodiment mode is different  
from that of Embodiment Mode 1 as follows: ~~the protective film 8~~ formed on the  
substrate 1 is formed of a stacked film having at least two or more layers which is  
15 provided with the lowest layer 7a made of an insulating compound and the upper layer 7b  
formed on the lowest layer 7a; the glass cap 8 that is bonded with the adhesive material 9  
is provided on the substrate 1; and outer surfaces of at least the organic thin film layer 3  
and the cathode 6 are sealed with the protective film 7 and the glass cap 8, whereby  
intrusion of moisture and oxygen into the organic thin film layer 3 and the cathode 6 are  
20 completely blocked.

[0101]

Operation of the organic electroluminescent element in this embodiment mode  
having the above structure is similar to the conventional example; therefore, description  
is omitted.

25 [0102]

According to this embodiment mode described above, intrusion of moisture and  
oxygen into the cathode 6 and the organic thin film layer 3 is completely blocked by the  
protective film made of a stacked film of at least two or more layers, which has an  
insulating compound layer 7 in the lowest layer, and the glass cap, whereby growth of  
30 dark spots in the light-emitting layer 5 can be suppressed.

[0103]

Further, the glass cap can prevent damage of the protective film, the cathode 6, the organic thin film layer 3, and the anode 2 due to external factor.

[0104]

- 5           In this embodiment mode, if the protective film has a two-layer structure of an insulating compound layer 7a and a metal film formed on the insulating compound layer 7a, the protective film can be formed easily, and decay in emission luminance with time can be prevented further effectively.

[0105]

- 10           Although this embodiment mode describes the case in which the organic thin film layer 3 has a two-layer structure of the hole transporting layer 4 and the light-emitting layer 5, the structure is not particularly limited to this as mentioned.

[0106]

- 15           The structure in Embodiment Mode 6 is specifically described. Two organic electroluminescent elements were manufactured in which the anode 2 made of an ITO film, the hole transporting layer 4 made of TPD, the light-emitting layer 5 made of Alq<sub>3</sub>, and the cathode 6 made of an Al-Li alloy are stacked on the glass substrate 1, similarly to the example of the above embodiment mode.

[0107]

- 20           As one of these, an organic electroluminescent element in a state before the shield member 8 is bonded was manufactured, in which a protective film made of a GeO film in a film thickness of 3 μm is formed by an ion beam sputtering method so as to seal at least the organic thin film layer 3 composed of the hole transporting layer 4 and the light-emitting layer 5 and the cathode 6 on the substrate 1. This is presented as  
25   Embodiment Mode 6.

[0108]

- Note that the GeO film was formed by a resistance heating deposition method because GeO and Ag can be deposited successively in the same deposition apparatus, and intrusion or attachment of dust to the protective film during deposition can be prevented.  
30   As a formation method of a GeO film, generally, an ion beam sputtering method can

reduce internal stress more greatly than a resistance heating deposition method.

[0109]

(Embodiment Mode 7)

Same as in Embodiment Mode 6, an organic electroluminescent element in a state before a shield member 8 is bonded was manufactured, in which a GeO film is formed in a film thickness of 1  $\mu\text{m}$  on a glass substrate 1 by a resistance heating deposition method so as to seal at least an organic thin film layer 3 composed of a hole transporting layer 4 and a light-emitting layer 5 and a cathode 6, and an Ag film is formed in a film thickness of 2  $\mu\text{m}$  on this GeO film by a resistance heating deposition method. This is presented as Embodiment Mode 7.

[0110]

Two kinds of organic electroluminescent elements were manufactured by forming the shield member by a similar method in that of Embodiment Mode 2.

[0111]

In the obtained two kinds of organic electroluminescent elements by the above method, a continuous emission test was conducted by supplying a constant current of 15  $\text{mA}/\text{cm}^2$  between the anode 2 and the cathode 6, so that change in emission luminance with respect to emission time was examined. A result thereof is described with reference to FIG. 9.

[0112]

FIG. 9 is a relation diagram of emission time and relative luminance in the continuous emission test. In FIG. 9, the relative luminance refers to the emission luminance expressed as a relative value at each light emission time in terms of light emission luminance of 1 upon start of continuous light emission test. As shown in FIG. 9, although Embodiment Mode 6 forms the protective film in a single layer of GeO film 3  $\mu\text{m}$  in the protective film, it was clear that decay in emission luminance with time is smaller in Embodiment Mode 7 having the protective film composed in two-layer structure of the GeO film and the Ag film.

[0113]

As the reason of such difference in characteristic, relation of thermal

conductivity of the GeO film and the Ag film is estimated as one factor. That is, the film composed of oxide or nitride is generally large in the internal stress as compared with metal film, and hence inferior in thermal conductivity. Therefore, as compared with Embodiment Mode 6, Embodiment Mode 7 is superior in thermal conductivity of protective film, and the heat generated by light emission is considered to be released smoothly outside through the protective film. In the organic electroluminescent element, if release of heat caused by light emission is poor, the organic thin film layer 3 is likely to deteriorate. Considering from such relation, it is estimated that decay in emission luminance with time is smaller in Embodiment Mode 7.

10 [0114]

In accordance with the above result, as the protective film 7, the luminous characteristic is excellent in the stacked structure of the lowest layer 7a that is an insulating compound layer made of oxide or nitride and the upper layer 7b made of a metal film, rather than a single layer of oxide or nitride. Furthermore, since the metal is superior in film forming property to the oxide or nitride, by defining the total film thickness of the protective film 7 in a range of 3  $\mu\text{m}$  to 30  $\mu\text{m}$ , in the structure comprising the insulating compound layer 7a formed in the lowest layer and the metal film 7b formed on the insulating compound layer 7, even when adhesiveness with the low-melting glass 9 is insufficient, growth of dark spots can be completely suppressed, and the organic electroluminescent element small in reducing of emission luminance can be realized.

20 [0115]

(Embodiment Mode 8)

Same as in the preceding example, an organic electroluminescent element was manufactured by stacking an anode 2 made of an ITO film, a hole transporting layer 4 made of TPD, a light-emitting layer 5 made of  $\text{Alq}_3$ , and a cathode 6 made of an Al-Li alloy on a glass substrate 1.

25 [0116]

On this glass substrate 1, a GeO film was formed in a film thickness of 1  $\mu\text{m}$  as a protective film on the cathode 6 in a resistance heating deposition apparatus so as to seal at least the organic thin film layer 3 composed of the hole transporting layer 4 and the

light-emitting layer 5 and the cathode 6, and an Ag film was continuously formed in a film thickness of 14  $\mu\text{m}$ .

[0117]

On the glass substrate 1 thus on which the protective film is formed, a glass cap  
5 of 1 mm thick formed from white sheet glass that has a depression with depth of 0.3 mm in the central part by a sand blasting method was cured to be bonded by being irradiated with 1 joule of ultraviolet ray, using an UV resin (Wardlock No. 856, manufactured by Kyoritsu Chemical Industries) as an adhesive, and an organic electroluminescent element as shown in FIG. 2 was obtained.

10 [0118]

This organic electroluminescent element was kept in a thermostatic cell controlled at 85 °C and humidity of 85%, and changes of shape of dark spots along with passing of the storage time were observed. In order to observe the change in shapes of dark spots with time, by taking out the organic electroluminescent element from the  
15 thermostatic cell every predetermined time and by making the organic electroluminescent element emit light in the same manner as in Embodiment Modes 6 and 7, the diameter of each dark spot was measured by microscopic observation, and the mean was calculated.

[0119]

(Comparative Example 2)

20 By way of comparison, an organic electroluminescent element was manufactured in the same manner as in Embodiment Mode 8 except that an Ag film was formed as the protective film, and this was presented as Comparative Example 2.

[0120]

The organic electroluminescence elements of Embodiment Mode 8 and  
25 Comparative Example 2 were kept in a thermostatic cell controlled at 85 °C and humidity of 90%, and changes of shape of dark spots with passing of the storage time were observed. To observe the changes of shape of dark spots with time, same as in the above method, the mean diameter of dark spots after passing a specific stand time was determined. The result is described with reference to FIG. 10.

30 [0121]

FIG. 10 is a relation diagram of storage time and mean diameters of dark spots in the storage test of the organic electroluminescence elements of Embodiment Mode 8 and Comparative Example 2. As shown in the diagram, in the extremely severe environments of 85 °C and humidity of 85% for the organic electroluminescent element, which is more difficult than in the evaluation condition in Embodiment Modes 6 and 7, it was cleared that growth of dark spots was hardly noted.

[0122]

As shown in this diagram, in the organic electroluminescent element of Embodiment Mode 8, as compared with Comparative Example 2, it was clear that the growth of dark spots was suppressed from the beginning of storage test.

[0123]

Thus, as compared with the conventional one using a protective film composed of oxide only, it was proved that growth of dark spots could be suppressed in this embodiment by using the protective film of stacked structure composed of an insulating compound layer 7 such as oxide formed in the lowest layer and a metal film formed on the insulating compound layer 7 and by bonding a shield material with low-melting glass.

[0124]

(Embodiment Mode 9)

FIG. 3 is a cross-sectional view of an essential part of an organic electroluminescent element in one embodiment mode of the present invention.

[0125]

In FIG. 3, reference numeral 10 denotes a carbon thin film, and a substrate 1, an anode 2, an organic thin film layer 3, a hole transporting layer 4, a light-emitting layer 5, a cathode 6, a protective layer 7, a shield member 8, and an adhesive layer 9 are same as mentioned above; therefore, the same reference numerals are used, and the description is omitted.

[0126]

An organic electroluminescent element of this embodiment mode is different from the conventional example in that the carbon thin film 10 is formed on an upper surface of the anode 2, and the anode 2 and the organic thin film layer 3 are bonded

through the carbon thin film 10.

[0127]

Since the carbon thin film 10 has lower work function than the mentioned anode, the energy gap with the organic thin film layer 3 is small, and a hole injecting property is improved, whereby luminance efficiency is increased. Further, the carbon thin film 10 has adhesiveness with the organic thin film 3 is more favorable as compared with that of the mentioned anode 2; therefore, it has superiority in uniform light-emitting characteristic and stability.

[0128]

Here, the carbon thin film is a thin film composed of carbon and, for example, formed by a sputtering method using carbon. Although the carbon target is not particularly defined, isotropic graphite, anisotropic graphite, carbon in glass form, or the like can be used, and particularly, isotropic graphite with high purity is suitable.

[0129]

When the carbon thin film is formed by a sputtering method, reactive sputtering is conducted in an atmosphere of mixed gas containing nitrogen or hydrogen and argon in order to control electric resistance.

[0130]

In a general thin film formation technique such as a sputtering method, a thin film with a film thickness of 50 angstrom or less has an island-shaped structure in film quality, so that a uniform film quality cannot be obtained. Therefore, electric resistance is increased in the film with a film thickness of 50 angstrom or less, and thus, current does not flow and light is not emitted.

[0131]

On the other hand, in a film with a film thickness of 1000 angstrom or more, the carbon thin film 10 becomes blackish, and accordingly, transmittance of EL light from the glass face is reduced.

[0132]

Here, blackness of the carbon thin film 10, that is, light absorption is effective for contrast up, and in considering the electric resistance, transmittance, and contrast, 50



angstrom to 500 angstrom is most suitable.

[0133]

Although FIG. 3 shows only a case of forming only the carbon thin film on the anode, the anode may be a single carbon thin film.

5 [0134]

Next, a specific structure of Embodiment Mode 9 is shown. Commercially available glass substrate with ITO (P110E-H-PX, manufactured by Nippon Sheet Glass CO., LTD) was etched with aqua regia so that the ITO was patterned into the desired pattern. After that, the glass substrate was cleaned ultrasonically with **agency(sic)**  
 10 (white 7-L, manufactured by UI kasei Co., Ltd.) for one hour, successively, cleaned ultrasonically with ion-exchange water for one hour, cleaned ultrasonically with acetone for 30 minutes, and cleaned ultrasonically with ethanol for one hour. Then, it was immersed in boiling ethanol for 5 minutes and dried naturally. The substrate that had been cleaned was set in a substrate holder in a DC magnetron sputtering apparatus  
 15 (730H, manufactured by Anelva Corporation), and the chamber was evacuated to the degree of vacuum of  $8 \times 10^{-7}$  Torr. After that, the carbon was sputtered to be deposited using a carbon target manufactured by Toyo Soda Manufacturing Co., Ltd. in pressure of nitrogen-argon mixed gas (nitrogen: 2.5 %) of 3m Torr at a substrate temperature of 150 °C. At this time, depending on sputtering time, three types of carbon films: two carbon  
 20 films with a film thickness of 50 angstrom; two carbon films with a film thickness of 100 angstrom; and two carbon films with a film thickness of 500 angstrom, were each manufactured.

[0135]

The substrate thereof is taken out of the chamber and set in a resistance heating  
 25 deposition apparatus, and the chamber is evacuated to the degree of vacuum of  $2 \times 10^{-6}$  Torr or less. After that, the hole transporting layer 4 with about 500 Å is formed using TPD as an evaporation source. Successively, the light-emitting layer 5 with about 750 Å is formed using Alq<sub>3</sub> as an evaporation source. Although the speed of deposition is not particularly limited, both deposition were performed at speed of 2Å/s at this time. Next,  
 30 the cathode 6 with a film thickness of 200 Å is formed using an AlLi alloy containing Li

at 15 at % as an evaporation source in the same vacuum layer. Then, the substrate 1 on which this element was formed was taken out of the vacuum chamber, and in each one of the three kinds of substrates, the shield member 8 was formed in the external side of the element by the following way.

5 [0136]

In an adhesive portion between the shield member 8 made from white sheet glass (thickness of 1 mm, manufactured by HOYA Corporation) and the glass substrate 1, a low-melting solder (Serasolza No. 123, manufactured by Asahi Glass CO., LTD) was attached in the conditions of frequency of 50 kHz and a heating temperature of 150 °C, using an ultrasonic soldering apparatus (Sun Bonder USM-IV, manufactured by Asahi Glass Co., Ltd). After that, the shield member 8 was fixed to the glass substrate 1, and the low-melting solder that had been attached to the white sheet glass was melted again in the conditions of frequency of 50 kHz, a heating temperature of 150 °C, and vibration added time of 20 to 30 seconds, using the ultrasonic soldering apparatus, so that the glass substrate 1 and the shield member 8 were bonded.

15

[0137]

By the above method, an organic electroluminescent element was manufactured, and this was presented as Embodiment Mode 9.

[0138]

20 Next, three kinds of organic electroluminescent elements in each of which the shield member 8 was formed were kept in environment at 60 °C and 90 % RH, and increase in portions where light is not emitted was observed.

[0139]

(Comparative Example 3)

25 An organic electroluminescent element, although it is similar to Embodiment Mode 9, in which a carbon film is not formed was manufactured for comparison, and this was presented as Comparative Example 3.

[0140]

The organic electroluminescent elements of Embodiment Mode 9 and Comparative Example 3 were kept in environment at 60 °C and 90 % RH for 100 hours,

30

and a state of increase in portions where light is not emitted from the initial state was observed. The result is shown in (Table 1).

[0141]

[Table 1]

	Carbon thickness	Initial emission (apply of 10 V)		After passing 100 hours at 60 °C and 90 % RH	
		Luminance variation	portions where light is not emitted	Luminance variation	portions where light is not emitted
Embodiment Mode 9	50 Å	±3 %	20 or less	±3 %	20 or less
	100 Å	±3 %	20 or less	±3 %	20 or less
	500 Å	±2 %	20 or less	±2 %	20 or less
Comparative Example 3	0 Å	±5 %	30 to 50	±5 %	30 to 50

5

[0142]

As shown in (Table 1), the organic electroluminescent element of Embodiment Mode 9 of the invention has luminance variation in the initial state of ±3 % or less and 20 or less portions where light is not emitted, whereas Comparative example 3 has

10

[0143]

In other words, adhesiveness between the anode and the organic thin film layer is increased by formation of the carbon film, and difference is generated in the luminance variation and the portions where light is not emitted as compared with the case where the

15

carbon film is not formed in the initial emission state.

[0144]

(Embodiment Mode 10)

An organic electroluminescent element was manufactured by a similar method to that of Embodiment Mode 1 except that a cathode is composed of 83 at% Al, 15 at% Li, and 2 at% Mg, and this was presented as Embodiment Mode 10. An initial light-emitting characteristic of the organic electroluminescent element and a mean diameter of a dark spot when being stored in environment at 40 °C and 90 % RH were observed.

10 [0145]

(Comparative Example 4)

An organic electroluminescent element was manufactured for comparison in the similar conditions to those of Embodiment Mode 10 except that the cathode is composed of 85 at% Al and 15 at% Li, and thus, this was presented as Comparative Example 4.

15 [0146]

(Comparative Example 5)

Furthermore, an organic electroluminescent element was manufactured in the similar conditions to those of Embodiment Mode 10 except that the cathode is composed of 83 at% Al, 15 at% Li, and 2 at% Zn, and this was presented as Comparative Example 5.

20 [0147]

Similar to Embodiment Mode 10, an initial light-emitting characteristic and a mean diameter of dark spot when being stored in the environment at 40 °C and 90 % RH were observed. The result is shown in FIGS. 13 and 14.

[0148]

25 FIG. 13 is a relation diagram between luminance and voltage in this embodiment mode of the invention, and FIG. 14 is a relation diagram between storage time and growth of dark spots in this embodiment mode of the invention.

[0149]

It is clear from FIG. 13 that the luminance characteristic in Embodiment Mode 10 using an AlLiMg alloy for the cathode 6 is improved as compared with the organic

30

electroluminescent element of Comparative Example 4 using an AlLi alloy for the cathode 6 and the organic electroluminescent element of Comparative Example 5 using an AlLiZn alloy for the cathode 6, whereas in the organic thin EL element of Comparative Example 5 using the cathode 6 in which Zn is added to the AlLi alloy, it seems that the luminance characteristic is reduced, and applied voltage of 2 to 3 V to Examples is seemed to be increased. This is considered that in a case of adding Mg to the AlLi alloy in the cathode 6, the work function is not increased, so that the luminance characteristic is hardly influenced; however, in a case of adding Zn, the work function is increased, so that the voltage is increased. In practice, work functions of the cathodes 6 having composition in Embodiment Mode 10, Comparative Example 4, and Comparative Example 5 were measured using AC-1 (manufactured by Riken Keiki Co., Ltd.). The respective work functions were 3.6 eV, 3.65 eV, and 3.8 eV, and it is considered that this difference indicates difference of voltage-luminance characteristics shown in FIG. X.

[0150]

However, as seen from FIG. 14 that a mean diameter of dark spot when being stored in the environment at 40 °C and 90 % RH had little difference among the organic electroluminescent elements of Embodiment Mode 10, Comparative Example 4, and Comparative Example 5. That is, the organic electroluminescent element of Embodiment Mode 10 has superiority in a light-emitting characteristic and storage stability.

[0151]

(Embodiment Mode 11)

FIG. 4 is a cross-sectional view of an essential part of an organic electroluminescent element in one embodiment mode of the invention, and FIG. 5 is a plan view of an organic electroluminescent element in one embodiment mode of the invention.

[0152]

In FIGS. 4 and 5, reference numeral 11 denotes an electrode driver line IC and reference numeral 12 denotes a lead line. A substrate 1, an anode 2, an organic thin film layer 3, a hole transporting layer 4, a light-emitting layer 5, a cathode 6, a protective layer

7, a shield member 8, and an adhesive layer 9 are the same as the mentioned ones; therefore, the same reference numerals are used, and description thereof is omitted.

[0153]

In FIG. 7 (sic), the organic thin film layer 3 is formed on the substrate 1 on which the anode 2 is formed, and the hole transporting layer 4, the light-emitting layer 5, and the cathode 6 are stacked on the organic thin film layer 3. The lead line 12 having a two-layer structure that is formed of a base layer and a conductive layer on the base layer is provided on the substrate 1 so as to connect the anode 2 or the cathode 6 with the electrode driver IC 11. A conductive layer material on the lead line is any one of copper, silver, gold, aluminum, iron, nickel, molybdenum, and platinum; an alloy thereof; or an alloy containing these metals, which has a function of extremely reducing electric resistance of the lead line.

[0154]

In accordance with this embodiment mode as described, the lead line is formed to have a two-layer structure that is formed of a base layer and a conductive layer formed on the base film, which has higher conductivity than the base layer, whereby resistance of the lead line is reduced, and the organic thin film electroluminescent element can be prevented from varying in emission luminance due to difference of ohmic loss in the lead line.

20 [0155]

Although the anode 2 and the cathode 6 are formed in liner shapes perpendicular to each other in Embodiment mode 11, it is not particularly restricted to this shape.

[0156]

After forming an ITO thin film of 0.16  $\mu\text{m}$  in film thickness on the glass substrate by a sputtering method, a resist material (OFPR-800 manufactured by Tokyo Oka Co., Ltd) was applied on the ITO film by a spin coating method to form a resist film of 10  $\mu\text{m}$  in thickness, and the resist film on the ITO film was patterned to a specified shape by masking, exposing and developing. This glass substrate was immersed in 50% hydrochloric acid at 60 °C, and the ITO film in the portion free from resist film was etched, and then the resist film was also removed, thereby obtaining a glass substrate on

which the anode made of the ITO film and a base layer of the lead line were formed. A resist material (OFPR-800 manufactured by Tokyo Oka Co., Ltd) was applied on only a portion where an organic thin film layer is formed on the glass substrate by a spin coating method to form a resist film of 10  $\mu\text{m}$  in thickness, and the resist film on the glass substrate was patterned to a specified shape by masking, exposing and developing. This glass substrate on which the resist film was formed was cleaned ultrasonically for 5 minutes with a detergent (Semico Clean, manufactured by Furuuchi Chemical Corporation), cleaned ultrasonically for 10 minutes in purified water, and immersed in a copper plating solution (new rare, manufactured by Okuno Chemical Industry Co., Ltd.) so that the base film was plated with a current density of 10  $\text{A}/\text{cm}^2$ , and a conductive layer made of copper in 2  $\mu\text{m}$  thickness was formed on the base layer of the lead line. The resist mask on the glass substrate on which this conductive layer was formed was removed. Then, the glass substrate was cleaned ultrasonically for 5 minutes with a detergent (Semico Clean, manufactured by Furuuchi Chemical Corporation), cleaned ultrasonically for 10 minutes in purified water, cleaned ultrasonically for 5 minutes in a solution of 1 part of ammonia water containing 1 part of hydrogen peroxide water and 5 parts of water, and cleaned ultrasonically for 5 minutes in purified water at 70  $^{\circ}\text{C}$ , sequentially, and moisture deposited on the glass substrate was removed by nitrogen blower, and it was heated and dried at 250  $^{\circ}\text{C}$ . The hole transporting layer was formed of a TPD thin film of 0.05  $\mu\text{m}$  in thickness by an evaporation method in a portion on the cleaned glass substrate where the anode was formed, and the light-emitting layer was formed of an  $\text{Alq}_3$  thin film of 0.075  $\mu\text{m}$  in thickness by an evaporation method on an upper surface of the hole transporting layer. After that, a predetermined mask is provided on an upper surface of the light-emitting layer, and the cathode was formed of a Mg-Ag alloy thin film of 0.25  $\mu\text{m}$  in thickness by a binary evaporation method. The electrode driver IC was mounted on the glass substrate on which the cathode was thus formed by a COG mounting method.

[0157]

Then, low-melting glass of Sn-P-Pb-O-F system (manufactured by Shoei Chemical Industries) ground to be powder of 10  $\mu\text{m}$  or less is mixed with methyl alcohol

at a concentration ratio of 1:1 by weight to form a paste, which is applied on white sheet glass of 1 mm in thickness manufactured by HOYA Corporation to be used as the shield member. In this white sheet glass, the portion confronting the forming portion of an organic electroluminescent element was drilled by 0.3 mm by a sand blasting method.

5 This can prevent breakage due to contact of the shield glass with the organic electroluminescent element. Instead of a sand blasting method, a honing method may be also employed. Next, in order to vaporize the organic solvent, after once drying for 10 minutes at 100 °C, it is then heated for 10 minutes in an electric furnace at 300 °C, and taken out and overlaid and adhered on the glass substrate 1 on which the element is  
10 formed. By this method, the organic electroluminescent element using glass in the shield member 8 by the above method can be completed.

[0158]

(Comparative Example 6)

As Comparative Example 6, an organic electroluminescent element in which a  
15 conductive layer was not formed was manufactured by a similar method to Embodiment Mode 16 (sic) except that copper was not plated on a base layer of a lead line.

[0159]

When the thus manufactured organic electroluminescent elements by Embodiment Mode 11 and Comparative Example 6 were driven with current voltage of  
20 10 V, difference of emission luminance in the light-emitting portion of the organic electroluminescent element manufactured by Embodiment Mode 11 was  $\pm 3\%$ , whereas emission luminance in the light-emitting portion of the organic thin film EL element manufactured by Comparative Example 6 was  $\pm 10\%$ .

[0160]

25 Further, there was not large difference of dark spots which had been stored at 60 °C and 90 %RH for 500 hours between the organic electroluminescent element manufactured by Embodiment Mode 11 and the organic electroluminescent element shown in Comparative Example 6.

[0161]

30 Accordingly, the invention described in Embodiment Mode 11 can obtain an



organic electroluminescent element with small luminance variation and excellent storage stability.

[0162]

[Embodiment mode 12]

5           After forming an ITO thin film of 0.16  $\mu\text{m}$  in film thickness on a glass substrate by a sputtering method, a resist material (OFPR-800, manufactured by Tokyo Oka Co., Ltd) was applied on the ITO film by a spin coating method to form a resist film of 10  $\mu\text{m}$  in thickness, and the resist film was patterned to a specified shape by masking, exposing and developing. This glass substrate was immersed in 50% hydrochloric acid at 60 °C, and the ITO film in the portion free from resist film was etched, and then the resist film was also removed, thereby obtaining a glass substrate on which the anode made of an ITO film and a lead line were formed. After the resist mask on the glass substrate was removed, the glass substrate was cleaned ultrasonically for 5 minutes with a detergent (Semico Clean, manufactured by Furuuchi Chemical Corporation), cleaned ultrasonically for 10 minutes in purified water, cleaned ultrasonically for 5 minutes in a solution of 1 part of ammonia water containing 1 part of hydrogen peroxide water and 5 parts of water, and cleaned ultrasonically for 5 minutes in purified water at 70 °C, sequentially, and moisture deposited on the glass substrate was removed by nitrogen blower, and it was heated and dried at 250 °C. In a portion on the cleaned glass substrate where the anode was formed, the organic thin film layer in which the TPD thin film of 0.05  $\mu\text{m}$  in thickness and the  $\text{Alq}_3$  thin film of 0.075  $\mu\text{m}$  in thickness were stacked was formed by an evaporation method. After that, a predetermined mask is provided on an upper surface of the  $\text{Alq}_3$  thin film, and the base layer was formed of an Al-Li alloy thin film of 0.25  $\mu\text{m}$  in thickness by a binary evaporation method. Further, a conductive layer was formed of an Ag thin film of 0.8  $\mu\text{m}$  in thickness on the base layer by an evaporation method, and the cathode having two-layer structure was formed on the organic thin film layer. The electrode driver IC was mounted on the glass substrate on which the cathode was thus formed by a COG (Chip On Glass) mounting method.

[0163]

30           The shield member thereafter was formed by the similar method to that of

Embodiment Mode 11.

(Comparative Example 7)

As Comparative Example 7, an organic electroluminescent element was manufactured by the similar method to that of Embodiment Mode 12 except that the cathode was a single layer without using the conductive layer.

[0164]

When the thus manufactured organic electroluminescent elements by Embodiment Mode 12 and Comparative Example 7, in which the cathode functions as a common electrode, were driven with current voltage of 5V, 8V, and 10 V, difference of emission luminance in the light-emitting portion of the organic thin film EL element in Embodiment Mode 12 was  $\pm 1\%$  in the case of any voltage, whereas emission luminance of the organic electroluminescent element in Comparative Example 7 was  $\pm 5\%$ .

[0165]

There was not large difference of dark spots which had been stored at 60 °C and 90 %RH for 500 hours between the organic electroluminescent element manufactured by Embodiment Mode 12 and the organic electroluminescent element shown in Comparative Example.

[0166]

Accordingly, the invention described in Embodiment Mode 12 can obtain an organic electroluminescent element with small luminance variation and excellent storage stability.

[0167]

(Embodiment Mode 13)

An organic electroluminescent element was manufactured by stacking an anode 2 made of an ITO film, a hole transporting layer 4 made of TPD, a light-emitting layer 5 made of Alq<sub>3</sub>, and a cathode 6 made of an Al-Li alloy on a glass substrate 1, and it was used in the backlight for liquid crystal display. The structure is shown in FIG. 11.

[0168]

FIG. 11 is a perspective view of an apparatus using the organic electroluminescent element of this embodiment mode of the invention in a display panel

for a backlight.

[0169]

The element of organic electroluminescence was formed in a multi-layer structure as shown below in order to obtain white light emission. First, in the manufacturing method, on a glass substrate 1 with ITO in a size of 52 mm × 15 mm × 1 mm, TPD as a hole transporting material was stacked in 500, oxazole complex of zinc as blue light-emitting layer 5 in 300, Alq<sub>3</sub> as green light-emitting layer 5 in 200, and Alq<sub>3</sub> doped with 1.5 mol. % of phenoxazone as red light-emitting layer 5 in 200, sequentially by vacuum resistance heating deposition method. In succession, an AlLi alloy of Li concentration of 10 at % as a cathode material was formed in 2000, and in the same chamber without breaking vacuum, germanium oxide (GeO) was formed in 5000, and it was taken out of the chamber. To seal this element, a 1 mm thick white sheet glass substrate 1 was used as shield member 8, and it was sealed by using low melting glass used in Embodiment Mode 1. Thus obtained organic electroluminescent element 20 in the drawing sealed with the shield member 8 was provided at the back side of the liquid crystal display unit, and a liquid crystal module was completed. In the drawing, reference numeral 16 is a chassis, 17 is a driver for controlling a liquid crystal display panel 19, and 18 is a metal frame on the outer circumference.

[0170]

In the conventional apparatus using a cold cathode-ray tube in the backlight, a diffusion plate is required to be provided at the back side of the liquid crystal display unit in order to make uniform the light-emission plane. By contrast, in the liquid crystal module of the invention using the organic electroluminescent element, since a diffusion plate is not required, a thin structure can be realized.

[0171]

In this embodiment mode, in order to obtain white light emission, the blue light-emitting layer, green light-emitting layer, and red light-emitting layer were stacked, but it is also no problem in the single-layer structure of mixing blue, green, and red pigments in the light-emitting layer 5. The light-emitting materials used for each color are not particularly limited, but oxadiazole derivative, tetraphenyl cyclopentadiene or the

like may be used as blue light-emitting material, or Alq<sub>3</sub> doped with DCM or the like may be used as red light-emitting material. In particular, when used in the display unit of portable backlight such as watch, calculator and telephone, white light is not always needed, and monochromic light of blue, green, or red may be used. Hence, the light-emitting layer 5 may be formed only of a material emitting each light.

[0172]

(Embodiment Mode 14)

FIG. 12 shows a perspective view of an apparatus using an organic electroluminescent element of this embodiment mode of the invention in a dot matrix type display panel.

[0173]

First, after forming an ITO film in a film thickness of 160 nm on a glass substrate 1 by a sputtering method, a resist material (OFPR-800, manufactured by Tokyo Oka Co., Ltd) was applied on the ITO film by a spin coating method, a 10 μm thick resist film was formed, and the resist film was patterned in a linear form of width of 300 μm and pitch of 400 μm by masking, exposing and developing.

[0174]

This glass substrate 1 was then immersed in 50% hydrochloric acid at 60 °C, and the ITO film in the portion free from forming of the resist film was etched, and the resist film was also removed to be used as anode, and the glass substrate 1 forming the ITO electrode patterned in a linear form in width of 300 μm and pitch of 400 μm was obtained.

[0175]

Next, this glass substrate 1 was cleaned ultrasonically for 5 minutes with a detergent (Semico Clean, manufactured by Furuuchi Chemical Corporation), cleaned ultrasonically for 10 minutes in purified water, cleaned ultrasonically for 5 minutes in a solution containing 1 part (by volume) of ammonia water, 1 part of hydrogen peroxide water, and 5 parts of water, and cleaned ultrasonically for 5 minutes in purified water at 70 °C, and water deposited on the glass substrate 1 was removed by nitrogen blower, then it was heated and dried at a temperature of 250 °C.

[0176]

On the ITO electrode side surface of the dried glass substrate 1, a TPD film was formed in a film thickness of about 50 nm as a hole transporting layer 4 in a resistance heating deposition apparatus evacuated to a degree of vacuum of  $2 \times 10^{-6}$  Torr or less.

[0177]

5        Next, similarly, in the resistance heating deposition apparatus, an  $\text{Alq}_3$  film was formed in a film thickness of about 75 nm as light-emitting layer 5 on the TPD film. The deposition speed of both TPD film and  $\text{Alq}_3$  film was 0.2 nm/s.

[0178]

Also in the resistance heating deposition apparatus, on the  $\text{Alq}_3$  film, using an  
10    Al-Li alloy containing 10 at % of Li as an evaporation source, a metal mask was disposed between the substrate 1 and the evaporation source, and an Al-Li alloy electrode as cathode 6 was formed in a width of 300  $\mu\text{m}$ , pitch of 400  $\mu\text{m}$ , and film thickness of 200 nm so as to be perpendicular to the ITO pattern. Further, on the Al-Li alloy electrode, a GeO film in a film thickness of 1  $\mu\text{m}$  and an Ag film in a film thickness of 10  $\mu\text{m}$  were  
15    sequentially stacked by an ion beam sputtering method, and a protective film 7 was formed.

[0179]

On the glass substrate 1 thus on which the protective film was formed, a glass cap of 1 mm thick white sheet glass forming a depression of 0.3 mm in depth in the  
20    central part by a sand blasting method, which was used as a shield member 8, was attached by curing by emitting 1 joule of ultraviolet ray, using an UV resin (Wardlock No. 856, manufactured by Kyoritsu Chemical Industries) as sealant, and a display panel was manufactured.

[0180]

25        In thus obtained display panel by the above method, by connecting a driver with the ITO electrode as the plus side and the Al-Li alloy electrode as the minus side, and applying a direct-current voltage or direct current in the selected anode 2 and cathode 6, the perpendicular portion emits light, so that it may be used as a display device of dot matrix type.

30    [0181]

## [Effect of the Invention]

Thus, according to the invention, by bonding a shield member glass or stainless steel to the substrate with low-melting glass or a low-melting solder, intrusion of moisture and oxygen into the cathode and the organic thin film layer can be completely blocked, growth of dark spots in the light-emitting layer can be prevented, and decay in emission luminance with time can be suppressed, so that it obtains excellent effects of notably enhancing the durability and reliability of the organic electroluminescent element. Besides, since damage of the protective film, the cathode, the organic thin film layer, and the anode due to external factors can be prevented, and it also gives an excellent effect of providing an organic electroluminescent element excellent in working efficiency in handling, storing, and conveying. Furthermore, by bonding the anode and the organic thin film layer strongly through the carbon film, reliability of the light-emitting characteristic is improved, and when the lead line and the cathode is covered with a material with excellent conductivity, light-emitting efficiency is enhanced. By using any one of an Al based alloy containing Mg, an Al based alloy containing Mg and Li, an Al based alloy containing Mn, and an Al based alloy containing Mn and Li as a material of the cathode, durability of the cathode is improved and reliability is enhanced.

[0182]

In accordance with the manufacturing method of an organic electroluminescent element of the invention, the shield member capable of completely blocking intrusion of moisture and oxygen into the cathode and the organic thin film layer can be formed easily with mass productivity, and the substrate and shield member can be bonded in an extremely short time and at a low heating temperature locally by using an ultrasonic wave or a laser beam, which gives an excellent effect of manufacturing the organic electroluminescent element excellent in durability and reliability with mass productivity and at low cost.

[0183]

In accordance with the display device of the invention, it gives an excellent effect of providing a display device with small decay in emission luminance with time and excellent in durability and reliability.

[Detailed description of the Drawings]

[FIG. 1] a cross-sectional view of an essential part of an organic electroluminescent element in one embodiment mode of the invention.

5 [FIG. 2] a cross-sectional view of an essential part of an organic electroluminescent element in one embodiment mode of the invention.

[FIG. 3] a cross-sectional view of an essential part of an organic electroluminescent element in one embodiment mode of the invention.

[FIG. 4] a cross-sectional view of an essential part of an organic electroluminescent  
10 element in one embodiment mode of the invention.

[FIG. 5] a plan view of an organic electroluminescent element in one embodiment mode of the invention.

[FIG. 6] a structural view showing a method for fusing an adhesive layer using a laser in one embodiment mode of the invention.

15 [FIG. 7] a relation diagram between storage time and growth of dark spots in embodiment mode of the invention.

[FIG. 8] a relation diagram between storage time and growth of dark spots in embodiment mode of the invention.

[FIG. 9] a relation diagram between emission time and relative luminance in  
20 embodiment mode of the invention.

[FIG. 10] a relation diagram between storage time and growth of dark spots in embodiment mode of the invention.

[FIG. 11] a perspective view of an apparatus in which an organic electroluminescent element in embodiment mode of the invention is used for a display panel for backlight.

25 [FIG. 12] a cross-sectional view of a liquid crystal lighting system in which an organic electroluminescent element in embodiment mode of the invention is used.

[FIG. 13] a relation diagram between luminance and voltage in embodiment mode of the invention.

[FIG. 14] a relation diagram between storage time and growth of dark spots in  
30 embodiment mode of the invention.

[FIG. 15] a cross-sectional view of an essential part of the conventional organic electroluminescent element.

[Description of Reference Number]

	1	substrate
5	2	anode
	3	organic thin film layer
	4	hole transporting layer
	5	light-emitting layer
	6	cathode
10	7	protective layer
	7a	lowest layer
	7b	upper layer
	8	shield member
	9	adhesive layer
15	10	carbon thin film
	11	electrode driver IC
	12	lead line
	13	YAG laser
	14	reflection mirror
20	15	lens

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(51) Int. Cl. <sup>6</sup>	Identification Mark	FI
H05B 33/26		H05B 33/26

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